

"The Evaporation of Water in a Current of Air." By EDGAR PHILIP PERMAN, Assistant Lecturer in the University College of South Wales and Monmouthshire. Communicated by Professor E. H. GRIFFITHS, F.R.S. Received February 4,—Read February 19, 1903.

Introduction and Historical.

It may be thought that so simple a matter as the evaporation of water in a current of air has already been thoroughly investigated, but, so far as I have been able to discover, this is not the case, although much concerning it has been taken for granted.

This research was undertaken in order to ascertain with what accuracy the vapour pressure of water could be calculated from the amount of water vapour carried off by an air current passed through the water, the temperature being maintained constant.

The work was begun in the Physikalisch-chemisches Institut, Leipzig, during the summer of 1902, and completed at University College, Cardiff, during the same year.

Experiments of a similar nature have been made by Regnault* and by W. N. Shaw.† Regnault found that the weight of the vapour drawn off agreed within about 1 per cent. with that calculated from the vapour pressure. The temperatures employed extended up to 45° C.

Shaw's experiments were at ordinary temperatures of the air, and a very close agreement was found between the usually accepted vapour pressures and those calculated from the amount of water vapour drawn off.

Description of Apparatus.

The apparatus employed consisted of the following chief parts:—

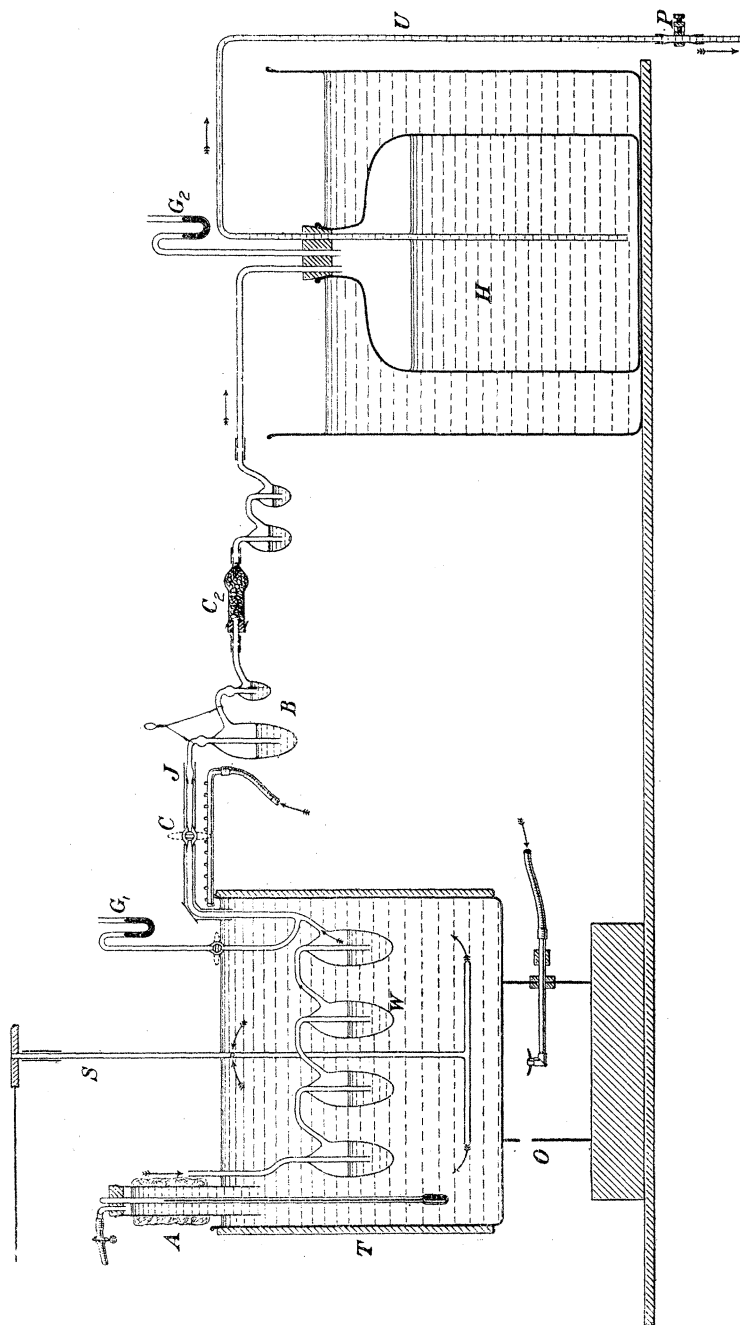
(1) Thermostat, with thermometer and stirring arrangement. (2) Four wash-bottles to contain the water. (3) Absorption apparatus to take up the water-vapour as the moist air passed through it. (4) Aspirator.

(1) The thermostat (T), consisted of an iron pot 23 cm. in diameter and 21 cm. high, surrounded by thick felt, and heated by an Ostwald burner (O), fig. 1. The thermometer was made by Fuess, of Berlin, and was standardised at the Reichsanstalt, Charlottenburg, number 17,000. It was divided into tenths of 1° C., and was read to 0.01°; the final corrections were also given to 0.01°. At the lower temperatures the stem was allowed to project from the bath just enough to make the thermometer readable, but at

* 'Mem. de l'Acad.,' vol. 26, p. 679.

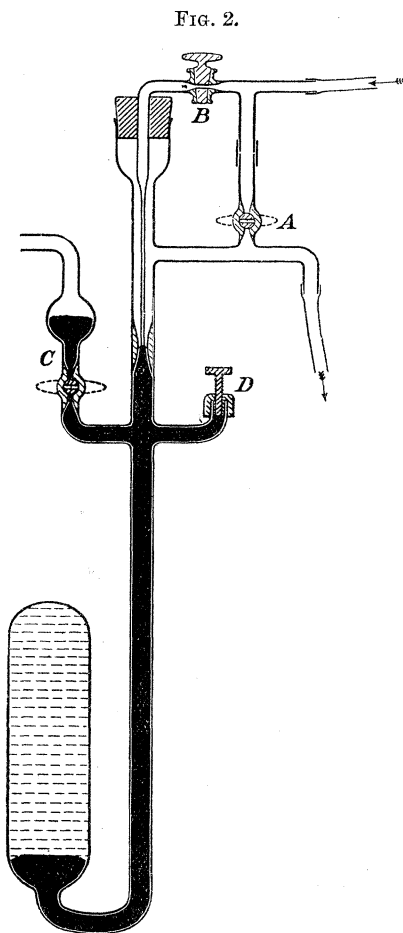
† 'Phil. Trans.,' A, vol. 179, 1888, Appendix No. III, p. 41.

FIG. 1.



the higher temperatures it was surrounded by a wide tube, open at the lower end, and closed by a cork at the upper end. The tube was wrapped round with a thick layer of cotton wool. The arrangement is shown in fig. 1, A. The liquid could be drawn up from the bath into the wide tube by means of a small tube passing through the

cork; the tube was then closed by means of a clip on a rubber tube connected with the glass tube. The temperature of the liquid in the wide tube was kept sufficiently uniform by convection currents. This was shown to be the case by emptying the liquid into the bath, and quickly drawing up a fresh portion, when the reading of the thermometer remained unaltered. In some of the experiments the thermometer was placed in a sloping position (in order to get the whole column into the bath); in that case a correction for internal pressure was made, being calculated from the coefficient given in the certificate. A toluol gas regulator was employed (not shown in fig. 1), which usually maintained the temperature constant to 0.01° ; it rarely varied more than this during an experiment, and I do not believe that the temperature error exceeds 0.02° in any single experiment. The regulator is of a new pattern, although it does not involve any new principle. The gas can be regulated in either direction by the stop-cocks



A, B, fig. 2. The quantity of mercury enclosed can be adjusted to suit any temperature over a wide range by means of the bulb C, and stop-cock beneath it, while, by means of the screw D, the temperature can be regulated to 0.01° , and can be easily brought to any desired point.*

* For details of the usual pattern of toluol regulator, see 'Physiko-chemische Messungen, Ostwald-Luther,' p. 88.

The stirring arrangement S, fig. 1, consists of a vertical glass tube, terminating in a horizontal T-piece open at both ends. In the vertical tube is an opening a little below the surface of the liquid. The T-tube was rotated about a vertical axis by means of a hot-air engine. The circulation of the water in the thermostat was found to be very effective when the T-piece made three revolutions a second.

(2) The wash-bottles, W, fig. 1, were each of about 100 c.c. capacity, and were all sealed together (except in some of the earlier experiments) in order to prevent leaks and the access of grease or other foreign matter. The last flask through which the air passed was connected with a pressure-gauge G_1 (read by a mirror scale) by a tube with a stop-cock just above the bath.

(3) The absorption apparatus, B, fig. 1, which was connected with the tube from W by a ground-glass joint J, consisted of two small wash-flasks containing pure concentrated sulphuric acid; about 10 c.c. were placed in the first flask and 2 c.c. in the second. In the earlier experiments the two flasks were connected by rubber tube, and weighed separately, but it was found that the second never gained more than 1 mg. during an experiment, and they were therefore sealed and weighed together. As a further proof of the completeness of the absorption, in two experiments at 80° a tube containing phosphoric anhydride was connected up with the second bulb, but it did not increase in weight by so much as 0.1 mg.

(4) The aspirator consisted of a large bottle, H, fig. 1, placed in a large pan of water. For the experiments at the lower temperatures the bottle had a capacity of 12 litres, but for some of the higher temperature experiments a 4-litre bottle was employed. The quantity of water outside was so large that the temperature did not change more than 0.1° during an experiment, and hence a regulator was considered unnecessary. Water was drawn off through the tube U into graduated flasks. The pressure of the air in the bottle H was read by means of a gauge, G_2 . Between the joint J and the bath, the projecting tube was surrounded by sheet brass and heated by a row of small gas jets (in the earlier experiments by a coiled wire, through which an electric current was passed), in order to prevent condensation of vapour in this part of the tube. The three-way stop-cock C was the dividing line between the flasks containing the water and the absorption apparatus; by means of it connection could be made between two U-tubes (not shown in the figure), containing strong sulphuric acid, and the absorption apparatus, so that the tube between B and C might be cleared of moisture by a current of air from the outside, passing first through the U-tubes.

Between the absorption apparatus and the aspirator were a calcium-chloride tube, Ca, and two small wash-bulbs containing water, the former to prevent water vapour from getting back to the absorption

apparatus, and the latter to saturate the air passing into the aspirator.

The weights employed were compared with a 1g. platinum weight, which had been standardised at the National Physical Laboratory. The balances employed were tested for inequality of length of arm, but in each case this was found to be negligible.

Method of Work.

An experiment was carried out as follows :—

The four wash-bottles were thoroughly cleaned by placing them in an inverted position and blowing steam through them for half an hour. This, or some similar process, is important, for if there is any grease present, erratic results are obtained. The flasks were then about two-thirds filled with distilled water, and placed in the thermostat.

The sulphuric acid was placed in the absorption apparatus, which was placed in position, and all necessary connections made. A slow stream of air was aspirated through the whole apparatus, and the two pressure gauges were read.

The absorption apparatus was weighed after standing in the balance case 15 or 20 minutes. Meanwhile the tube CJ was cleared of moisture. The absorption apparatus was then connected up again, the rubber junctions coated with wax, the pressure in the aspirator adjusted to that previously found, and the apparatus was left for some minutes to discover any possible leak. The absence of any leak being proved, the clip P and the stop-cock C were opened and the experiment begun.

To bring the experiment to an end, the clip P was first closed, and then the stop-cock C. The pressure gauge G_2 was read again (it usually remained quite unaltered), and the moisture was driven from the tube CJ into the absorption apparatus (by the method already described), which was then removed to be weighed.

The temperature of the aspirator and the barometer were read during the experiment.

At the lower temperatures the air was never passed through at a greater rate than 0.1 litre per minute, while at the higher temperatures the rate was not more than 0.05 per minute. The air acquires the temperature of the bath and becomes saturated with aqueous vapour with surprising rapidity. Special experiments were made to test this point.

Saturation of the Air.

If air is passed through *one* wash-bottle only, containing water, and placed in a thermostat at a temperature higher than that of the air, a rapid fall of temperature takes place owing to the low temperature of the air and to the cooling by evaporation of the water. Experiments were made at 40° C. and at 76° C.; a thermometer which could be

read to 0.01° was placed in the wash-bottle through a cork in the neck, and air was drawn through at varying rates. In most of the experiments the air passed first of all through another wash-bottle containing water, and then through the flask containing the thermometer. The results are here tabulated :—

Temperature of thermostat.	Wash- bottle.	Air current.	Fall of temperature.
40° C.	1	0.16 l. per min.	0.12° in 5 mins.
40	1	3.0 "	0.82 "
40	2	0.6 "	No fall.
40	2	3.0 "	"
76	2	0.05 "	"
76	2	0.08 "	"
76	2	0.14 "	"
76	2	0.50 "	Slow fall.
76	2	0.86 "	Rapid fall.

It will be noted that at 40° , with only two flasks, no perceptible fall of temperature is produced by such a rapid current of air as 3 litres per minute, while at 76° , with the same number of flasks, a current of 0.14 litre per minute has no perceptible effect. Since the rates used in the actual experiments for the determination of vapour pressure were much less than 0.14 litre per minute, and four flasks (in some cases five) were employed, there can be no doubt as to the saturation of the air in these experiments.

This was confirmed also by varying the rate during the experiments, when the variation was not found to have any effect on the amount of water driven off.

Method of Calculation.

An experiment carried out in the manner described furnishes the following data :—

W = Weight of water drawn off.

P = Pressure in the last aspiration flask.

T = Absolute temperature of air in aspirator.

V = Volume of air drawn through the water, measured at temperature and pressure of aspirator.

p = Pressure of air in aspirator.

If we assume that the vapour pressure of water is the same in the presence of air as in the absence of air or any other gas, and that the partial pressure of each constituent of the gaseous mixture is the same as if each occupied the whole space (Dalton's laws), and also that the density of saturated water vapour is normal, then the vapour pressure can be calculated from the relation

$$\frac{\text{Pressure of aqueous vapour}}{\text{Total pressure}} = \frac{\text{Volume of aqueous vapour}}{\text{Total volume}}$$

The "normal" value of the density of aqueous vapour is taken to be that calculated from the density of oxygen* and the molecular weight of water, and the corresponding specific volume, which is more convenient for purposes of calculation, is 1.242. The vapour pressure is calculated then from the expression—

$$\frac{1.242 \times 760 \text{ W.P.T}}{T(1.242 \times 760W) + 273.V.p.}$$

Results.

The lowest temperature at which the method was applied was 20° C. The experiments are naturally very tedious at low temperatures owing to the large volume of air which must be passed through the apparatus. The whole of the experimental results are here tabulated, the actual data being given in an Appendix.

It will be noted that the temperatures are at exactly every 10° (with two exceptions); the corrections were calculated beforehand, and the thermostat carefully adjusted. One exception is 80.10°, which was the temperature in the only series of experiments made with a portion of the thermometer stem outside the bath; a correction was made for this exposed portion in the usual way. On calculating out the results, the vapour pressure appeared to be abnormally high, and consequently a large number of experiments were made to ascertain this point with certainty. However, on proceeding to 90°, normal vapour pressures were again obtained, and suspicions were aroused as to the exactness of the temperature reading at 80°. The thermostat was brought again to 80°, and the thermometer placed first with its stem surrounded by the wide tube and hot liquid, and then placed in the original position, when it was found that the correction had been over-estimated by 0.1°. The reason for this large difference between the calculated and the real correction is probably that in this class of thermometer the column of mercury projecting from the thermostat is surrounded by a bath of hot air enclosed by the outer tube of the thermometer. The other exception, at 40.66°, was one of the earliest experiments carried out.

The vapour pressures given in the last column are taken from Ostwald and Luther's 'Physiko-chemische Messungen' (1902), p. 156. The numbers were obtained by plotting the differences between the results of Wiebe (76° to 100°) and Thiesen and Scheel (−10° to +25°), and the Regnault-Broch numbers, interpolating the curve from 25° to 76°, reading off the corrections from the smoothed curve, and applying them to the Regnault-Broch numbers throughout.

* The weight of a litre of oxygen has been taken as 1.4295 g.

Temperature.	Vapour-pressure. mm.	Mean vapour-pressure.	Vapour-pressure. Regnault corrected.
20° C.	17·61		
	17·69	mm.	mm.
	17·53	17·61	17·52
	17·62		
30	31·89		
	31·81		
	32·05	31·88	31·73
	31·79		
40·66	57·45		
	57·36		
	57·34	57·34	57·15
	57·33		
	57·23		
50	92·34		
	92·33		
	92·38	92·39	92·35
	92·50		
60	148·8		
	149·1		
	148·5	148·94	149·3
	149·2		(Regnault uncorr.)
	149·1		148·9
70	234·2		
	233·2		
	234·5		
	235·0	233·98	234·0
	233·5		
	233·5		
80·10	358·1		
	356·6		
	358·4		
	357·4		
	357·9	357·1	356·9
	355·0		
	357·1		
	357·6		
	356·1		
90	526·4		
	525·6		
	527·6	526·3	525·8
	525·7		

It must be here remarked that the experiments at the lower temperatures are by no means so reliable as those at the higher temperatures, for the following reasons:—

(1) They were the first carried out, before experience in working the experiment had been gained.

(2) The amount of water carried over was always very small, so that it is impossible for these experiments to be so accurate as those in which the water is carried off more rapidly.

(3) A rubber connection was used at J (fig. 1), whereas in the later experiments this was replaced by a ground-glass joint. Also, the absorption flasks were weighed with glass stoppers connected by rubber tubes, and it was found that moisture from the air found its way slowly through the rubber, although the glass tubes were made to touch. The absorption apparatus was in this way found to take up sometimes as much as 0.5 mg. in an hour, which is quite sufficient to account for the highness of the numbers obtained in these experiments. This may be, perhaps, included under reason (1).

At the higher temperatures there was no rubber connection through which moisture could pass to the absorption apparatus, and the apparatus was closed with small rubber stoppers inserted into the tubes. With this arrangement the weight was found to be constant.

Deductions from Experimental Results.

The vapour pressures obtained are seen to agree very closely with those obtained by direct measurement. Now, in the calculation, certain assumptions have been made, viz., Dalton's law of partial pressures, and that the density of aqueous vapour is normal. It would thus seem that these assumptions are justified. It is highly improbable that deviations from Dalton's law, and from the normal density, should so balance one another at all these temperatures as to give correct vapour pressures. Fortunately there is independent evidence of the validity of Dalton's law under the conditions of the experiments. Galitzine,* by some well-devised experiments, showed that there was no appreciable deviation from Dalton's law for air and aqueous vapour at moderate pressures below 100° C.

It may be concluded, then, that the density of saturated water vapour at the pressures and temperatures employed is very near the normal value. This conclusion seems to the author quite justified by the experiments described, although it is at variance with the work of a number of other investigators, who have found the density to be greater than normal, usually from 1 to 2 per cent., sometimes much more.

* 'Wied. Ann.,' 1890, vol. 41, p. 588

A list of papers on the subject is here given for reference :—

Regnault ('Ann. Chim. Phys.' (3), 15, 129, 1845).

Fairbairn and Tate ('Phil. Trans.,' vol. 150, p. 185, 1860).

Wüllner and Grotrian ('Wied. Ann.,' vol. 11, p. 544, 1880).

Perot ('Comptes Rendus,' vol. 102, p. 1369, 1886).

Batelli ('Mem. dell' Accad. di Torino,' (2), vol. 41, p. 33, 1891, and (2), vol. 43, p. 1, 1892).

Ramsay and Young ('Phil. Trans.,' A, 1892, p. 107).

Bauer ('Wied. Ann.,' vol. 55, p. 184, 1895).

Griffiths* has calculated the density of saturated water-vapour from latent heat of evaporation by means of the thermo-dynamical equation

$$L = \frac{T}{J} (s' - s) \frac{dp}{dT}.$$

The values of dp/dT were taken from Broch's reduction of Regnault's experimental results; the author has recalculated the densities, replacing these values of dp/dT by numbers calculated from the vapour pressures given by Luther.† Both series are given in the following table :—

Temperature.	Regnault.	Density.	Regnault corrected.	Density.
0°	0·330	0·6184	0·340	0·6002
20	1·073	0·6215	1·031	0·6169
40	2·936	0·6270	2·942	0·6257
60	6·922	0·6298	6·927	0·6293
80	14·388	0·6305	14·35	0·6323
100	26·981	0·6299	27·20	0·6248
				Mean 0·6215

This method is a very indirect one, but is free from the errors involved in most of the experimental methods. Since L and J have been determined with great accuracy, the densities calculated from them should be accurate at the higher temperatures where dp/dT is known with fair accuracy. The mean density so obtained is very close to the normal density, 0·6227.

I believe the greater number of the experiments quoted are rendered inaccurate by the condensation of vapour on the sides of the glass vessel employed, owing to the hygroscopic nature of lass; this is impossible to avoid, but in my experiments it will have

* 'Phil. Trans.,' A, vol. 186, 1895, p. 325.

† 'Physiko-chemische Messungen,' Ostwald-Luther, p. 156.

no effect on the result, and I believe it can be safely concluded from these experiments that the density of saturated water vapour under the conditions of the experiment (that is, when mixed with half its volume to forty times its volume of air, at temperatures from 90° to 20°) is normal.

Also, it is highly improbable that the density of the saturated vapour alone is more than slightly above normal at these temperatures, as the deviations from Dalton's law have been shown to be very small. This is also confirmed by the results of Griffiths (*vide supra*).

Summary and Conclusion.

(1) When air is aspirated through water, it becomes saturated with aqueous vapour with great rapidity.

(2) In the saturated air so obtained, the pressure of the aqueous vapour is the same as the vapour pressure of water when no other gas is present.

(3) The density of the aqueous vapour in the mixture is normal.

(4) The density of saturated aqueous vapour (without admixture) is probably only very slightly (if at all) above normal at temperatures up to 90° .

APPENDIX.
Experimental Data.

Temperature of water.	W.	P.	T.	V.	p.	Vapour pressure.
	grammes.	mm.	C°.	litres.	mm.	
20° C.	0·1744	735·7	290·8	10	715·2	17·61
	0·1752	740·6	291·0	10	720·1	17·69
	0·1735	739·7	291·0	10	719·2	17·53
	0·1746	735·0	291·0	10	715·0	17·62
30 	0·3213	739·4	291·0	10	717·3	31·89
	0·3215	740·4	291·1	10	718·2	31·81
	0·3225	737·4	291·3	10	714·8	32·05
	0·3194	743·9	292·0	10	722·3	31·79
40·66	0·3030	745·3	289·5	5	726·4	57·45
	0·3075	739·0	286·2	5	723·0	57·36
	0·3033	732·7	289·1	5	714·1	57·34
	0·3021	736·8	289·8	5	717·1	57·33
	0·3013	737·5	290·1	5	718·0	57·23
50 	0·5104	737·9	290·7	5	717·3	92·34
	0·5095	737·7	291·0	5	716·8	92·33
	0·5108	737·5	290·5	5	716·8	92·38
	0·5114	737·5	290·8	5	716·6	92·50
60 	0·8866	738·4	294·3	5	715·1	148·8
	0·8893	739·5	294·3	5	716·2	149·1
	0·8820	738·5	295·0	5	714·4	143·5
	0·8921	738·0	294·2	5	715·8	149·2
	0·9032	739·7	291·0	5	720·2	149·1
70 	0·6802	745·9	285·0	2·005	730·1	234·2
	0·5878	745·2	285·3	1·747	728·4	233·2
	0·6768	750·4	285·3	2·005	732·6	234·5
	0·6785	750·4	285·5	2·005	732·4	235·0
	0·6610	761·7	287·8	2·005	742·1	233·5
	0·6616	760·9	287·9	2·005	742·0	233·5
80·10	1·3616	754·1	284·8	2·004	739·5	358·1
	1·3626	735·1	287·4	2·004	717·3	356·6
	1·3870	729·2	287·4	2·004	711·4	358·4
	1·3887	728·2	286·4	2·004	711·7	357·4
	1·3642	746·7	285·6	2·020	730·3	357·9
	0·6672	752·9	285·8	1·003	736·7	355·0
	1·3526	753·2	284·9	2·004	737·6	357·1
	1·3502	754·3	285·7	2·004	738·2	357·6
	1·3413	753·3	285·7	2·004	737·2	356·1
90 	3·4143	756·9	286·7	2·004	739·5	526·4
	3·4420	755·5	284·9	2·004	739·6	525·6
	3·4835	753·1	286·6	2·004	735·9	527·6
	3·4036	756·1	287·0	2·004	738·6	525·7